862. *Dimethylberyllium. Part II.* Co-ordination Compounds.*

By G. E. Coates and N. D. Huck.

Dimethylberyllium forms co-ordination compounds with trimethylamine, trimethylphosphine, and dimethyl and diethyl ether, but not with trimethylarsine or dimethyl sulphide. The properties of these indicate that the order of stability of the compounds is $N > P > O$. Whereas the co-ordination affinity of trimethylamine to dimethylberyllium is more than sufficient to break down the polymeric structure of the latter, forming the volatile substance $\mathrm{Me_2\overset{-}{Be}{-}\overset{+}{N}Me_3}$, there is evidence to show that weaker donor molecules such as trimethylphosphine have a co-ordination affinity similar in magnitude to the affinity of dimethylberyllium molecules for each other; the latter situation results in the formation of a number of co-ordination compounds with various Be : P ratios, and in some rather peculiar properties shown by dimethylberyllium–trimethylphosphine and –dimethyl ether systems. The formation of an unstable compound $\mathrm{(Me_2Be)_2(NMe_3)_3}$ has been demonstrated; this is interpreted on the basis of half-bonding between one nitrogen and two beryllium atoms.

THE strongly electron-deficient nature of dimethylberyllium (see Part I *) should permit the formation of a series of stable co-ordination compounds, for example, with the donor elements of Groups V and VI of the Periodic Table. In this respect dimethylberyllium

* Part I, preceding paper.

might be expected to behave like trimethylaluminium (Brown and Davidson, *J. Amer. Chem. Soc.*, 1942, **64**, 316) and trimethylgallium (Coates, *J.*, 1951, 2003), which form 1 : 1 co-ordination compounds, $Me_3\overset{-}{Al}-\overset{+}{P}Me_3$ being a typical example. In fact, however, the situation is very much more complex with dimethylberyllium, which forms more than one compound with each donor molecule with which it combines. This paper is concerned only with donor molecules containing no reactive hydrogen atom, since donor molecules such as alcohols and secondary amines react with dimethylberyllium to form methane and associated hydroxy- or amino-beryllium compounds which will be the subject of Part III. The donor molecules studied were trimethylamine, trimethylphosphine, trimethylarsine, dimethyl and diethyl ether, and dimethyl sulphide.

EXPERIMENTAL

All the experiments were conducted in a high-vacuum apparatus of standard design. Materials were prepared and purified as described in Part I of this series and in Part I of the trimethylgallium series (Coates, *loc. cit.*). Dimethylberyllium, prepared from metallic beryllium and dimethylmercury, was separated from mercury by solution in dry ether followed by filtration through a grade-4 sintered disk and subsequent removal of ether in a high vacuum. Most of the co-ordination equilibria were studied in the " high-temperature bulb " (Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780; Sanderson, " The Vacuum Manipulation of Volatile Compounds," Wiley, 1948). For convenience, quantities of materials used in experiments are usually given in normal c.c. (N-c.c.), *i.e.*, the volume which the (monomeric) vapour would occupy at N.T.P.

Trimethylamine.—Dimethylberyllium–trimethylamine. Dimethylberyllium (about 180N-c.c.) was sublimed into a reaction bulb and cooled in liquid oxygen. Trimethylamine (238N-c.c.) was condensed on the dimethylberyllium, and the reaction bulb allowed to warm to room temperature; the ensuing reaction was quite mild since no visible change was observed. The excess of trimethylamine (64N-c.c.; v. p. 678 mm. at 0°) was passed through a trap cooled to –60° and collected at –183°; thus 174N-c.c. had reacted. A little of the white crystalline product had condensed in the trap cooled to –60°, but most remained in the reaction vessel; it was distilled into a number of small sample bulbs cooled in liquid oxygen and sealed. On slow cooling of the warm *product*, large colourless rhombic crystals, m. p. 36°, were formed, which reacted vigorously with air and moisture, forming dense white clouds of beryllium oxide and hydroxide and liberating trimethylamine.

The contents (0·2301 g.) of one of the sample bulbs were cautiously hydrolysed by water, followed by hydrogen chloride, in the vacuum apparatus. Methane (identified by vapour pressure, 105·2 N-c.c.) was pumped into a gas burette through a liquid-oxygen trap by means of a Töpler pump, and the trimethylamine (0·1373 g.) was estimated by distillation into standard acid in the usual way [Me_2Be,NMe_3 (0·2301 g.) requires CH_4, 105·0N-c.c.; NMe_3, 0·1385 g.].

The vapour pressure, given for various temperatures in Table 1, cannot be represented by any simple equation of the type, $\log_{10}p = -A/T + B$, since the slope of the log p–T^{-1} graph varies with temperature in the sense that the apparent latent heat of vaporisation decreases much more rapidly than usual with increasing temperature. No decomposition occurred during these measurements. The vapour pressure of the solid corresponds to a latent heat of sublimation of 20 ± 1 kcal./mole, that of the liquid corresponds to a latent heat of evaporation of about 12 kcal./mole at 50° and about 8 at 130°. The molecular weights, from measurement of the temperature and pressure of a known weight (0·1395 g.) in the high-temperature bulb, are given in Table 2. The compound is thus monomeric at higher temperatures, but shows signs of association.

TABLE 1.

Temp. (c)	26°	30°	32°	36°	42°	48°	56°	64°
V. p. (mm.)	1·34 *	1·83 *	2·65 *	3·92 *	5·7	8·1	12·5	18·4
Temp. (c)	72°	80°	90°	100°	110°	120°	130°	140° †
V. p. (mm.)	26·2	36·6	53·7	76·6	101·2	137·4	178·5	222·0

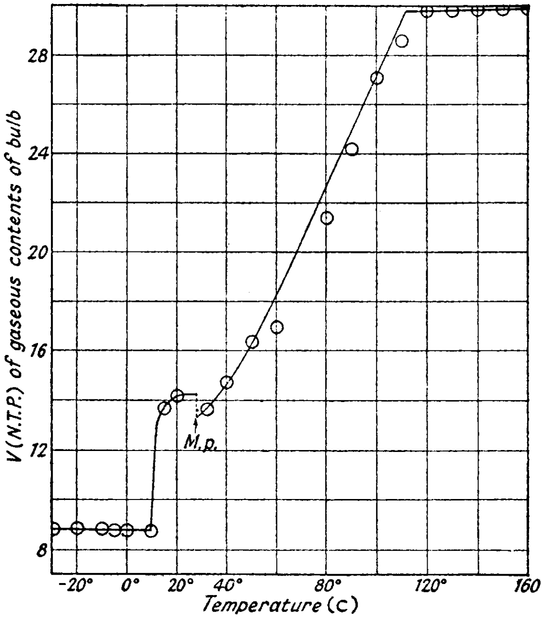
* Solid. † Sample volatilised completely at higher temps.

TABLE 2.

Temp. (c)	150°	155°	160°	170°	180°
M	105·3	104·5	103·7	102·1	100·5
Degree of association	1·073	1·065	1·056	1·040	1·024

Bisdimethylberyllium–tristrimethylamine. Dimethylberyllium–trimethylamine (14·20N-c.c.) was condensed in the high-temperature bulb (182·2 c.c.) and followed by trimethylamine (15·84N-c.c.). The gas pressure in the bulb was measured between −30° and +170°; reproducible results were obtained with both heating and cooling. In Fig. 1 the volume of the gaseous contents of the bulb, reduced to N-c.c., is plotted against temperature (for one experiment). From −30° to +27° the bulb contained solid and gas only. From −30° to +9·4° the gas pressure followed Charles's law, *i.e.*, the volume reduced to N-c.c. was constant (8·80N-c.c.). Since the total quantity of trimethylamine in the system was 14·20 + 15·84 = 30·04N-c.c., it follows that the solid phase contained 14·20N-c.c. of dimethylberyllium combined with 30·04 − 8·80 = 21·24N-c.c. of trimethylamine. The ratio of trimethylamine to dimethylberyllium in the solid phase was therefore 1 : 21·24/14·20, or 1 : $1\cdot49_6$, and the formula of the solid $(Me_2Be)_2(NMe_3)_3$. On heating from lower temperatures there was a very sudden increase of pressure at 9—10° followed at about 27° by melting of the solid; this was not sharp, since some evolution of trimethylamine from the compound $(Me_2Be)_2(NMe_3)_3$ had already occurred. The melting was always accompanied by a slight pressure drop which is a strong indication that the extra molecule of trimethylamine is not held as a lattice compound. With increasing temperature the pressure steadily increased, owing both to the further dissociation of the (now liquid) 2 : 3 compound and to the vaporisation of the 1 : 1 compound, until from 120° to 170° the contents of the bulb were entirely gaseous and of constant volume (reduced to N.T.P.) of 29·9N-c.c. This corresponds within experimental error (including deviations from the simple gas law) to 14·20N-c.c. of Me_2Be,NMe_3 originally introduced, together with the 15·84N-c.c. of trimethylamine added.

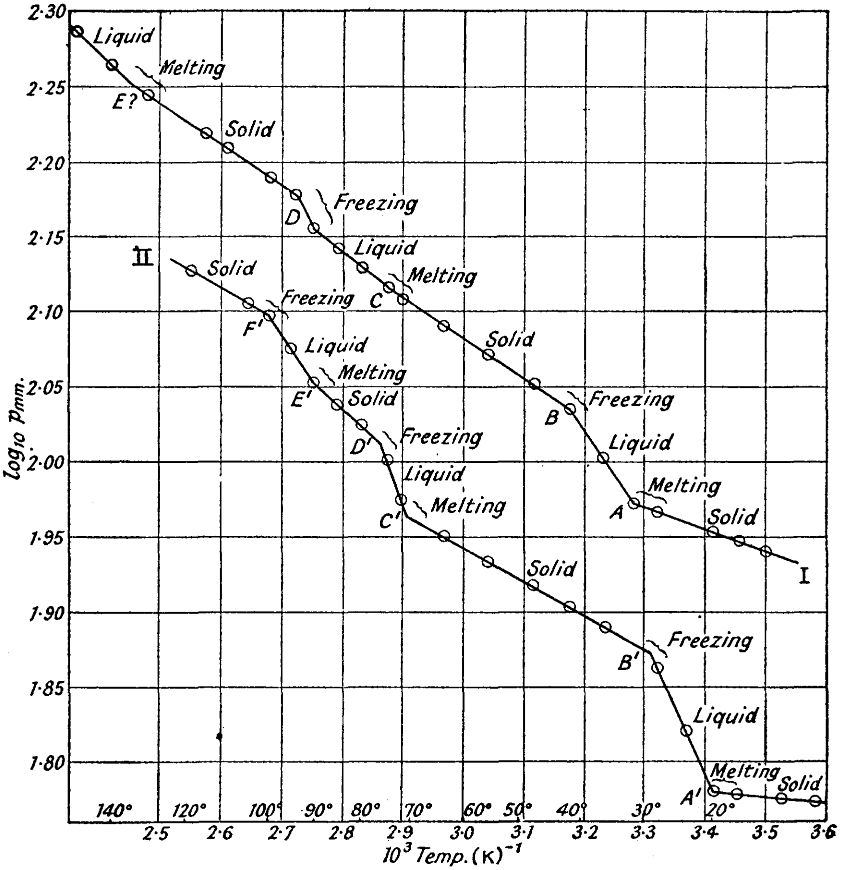
FIG. 1. Me_2Be,NMe_3 (14·2N-c.c.) + NMe_3 (15·8N-c.c.).



Trimethylphosphine.—Interaction with trimethylphosphine was much more complicated. Preliminary experiments showed that trimethylphosphine is a weaker donor toward dimethylberyllium than is trimethylamine; at room temperature, at which dimethylberyllium is virtually non-volatile, all the trimethylphosphine could be separated by pumping in a high vacuum. However, it was evident from measurements of the amounts of trimethylphosphine present in the condensed state (at pressures well below the saturation pressure of trimethylphosphine vapour) that a considerable range of compounds $(Me_2Be)_x(PMe_3)_y$ is formed, each one being stable only in a certain range of temperature and pressure of trimethylphosphine.

The results of two typical experiments are shown graphically in Fig. 2 (I and II). For the first of these, dimethylberyllium (3·79N-c.c., this quantity, being too small to weigh accurately, was determined from the volume of methane, 7·58 ± 0·05N-c.c., liberated on hydrolysis at the conclusion of the experiments) was transferred to the high-temperature bulb and an excess of trimethylphosphine (24·0N-c.c.) was added. As the mixture warmed from −183° no reaction was observed until about −25° when colourless rhombic crystals slowly formed from the original fine white needles of dimethylberyllium, liquid trimethylphosphine being present at this temperature. The variation of pressure with temperature on continued heating to 160° is shown in Fig. 2 (I), in which $\log_{10}$ pressure (mm.) is plotted against (temp., K)$^{-1}$ × 10^3. This form of representation is preferred since it shows the characteristic discontinuities better than others, and both a dissociation equilibrium and, over a limited temperature range, the change of pressure of gas with temperature, give an approximately linear relation between $\log p$ and T^{-1} [in fact, for Charles's law, $d \log p/d(1/T) = -T$]. Pressure changes were followed both on heating and cooling; equilibrium was established rather slowly, and a single (heating) run usually took 11—12 hours. Equilibrium on cooling was attained even more slowly, and since the same phenomena were then observed in the reverse order, the latter data are not recorded in detail.

FIG. 2.



Dimethylberyllium (3·79N-c.c.) + (I) *trimethylphosphine* (24·0N-c.c.).
,, . ,, + (II) *trimethylphosphine* (18·5N-c.c.).

The crystalline solid which formed at ~ −25° melted at 27—31°, with a subsequent rapid pressure increase. The composition of this solid [Fig. 2 (I), point *A*] was $Me_2Be(PMe_3)_2$, since the volume of the gaseous contents of the bulb was 16·4N-c.c., so 24·0—16·4 = 7·6N-c.c. of trimethylphosphine were combined with 3·79N-c.c. of dimethylberyllium. The composition of the solid was very nearly constant at a Be : P ratio of 1 : 2 from temperatures near the condensation point of trimethylphosphine to point *A*. The increase of slope of the plot must be due to the decomposition of this compound with evolution of trimethylphosphine. As the temperature was increased the liquid gradually froze again, becoming completely solid just below

50°, when its composition (point *B*, from the volume of gaseous trimethylphosphine) was $(Me_2Be)_2(PMe_3)_3$. At this point the rate of increase of pressure with temperature suddenly decreased. This new solid melted at about 70—75° when there was another change of slope; at this stage, point *C*, the composition of the condensed phase was approximately Me_2Be,PMe_3. This, however, provides hardly any evidence for the existence of a 1 : 1 compound; the latter, however, is more clearly indicated in Fig. 3 and was definitely proved by experiments at constant temperature mentioned below. Between 90° and 95° the liquid froze again, and when it became completely solid (point *D*), its composition was $Me_2Be(PMe_3)_{0\cdot63}$, *i.e.*, corresponding to an empirical formula $(Me_2Be)_3(PMe_3)_2$. At these higher temperatures it may not be justifiable to neglect the vapour pressure of the co-ordination compounds themselves, although these are likely to be small compared with the total pressure (100—200 mm.) of trimethylphosphine present. The third solid, $(Me_2Be)_3(PMe_3)_2$, melted rather gradually between 130° and 140° and the liquid finally crystallised again at 160°. In these last stages the volume of combined trimethylphosphine is so small (of the order of 1 c.c.) and the vapour pressure even of dimethylberyllium becomes quite appreciable (*e.g.*, 10 mm. at 140°) that it is not possible to follow the composition of the condensed phase.

Fig. 2 (II) refers to an experiment in which a smaller proportion of trimethylphosphine is present; at any temperature the pressure of the latter is less than in the experiment to which Fig. 2 (I) refers, and the changes of slope are more pronounced. A very similar sequence of events occurred, but the points *A'*, *B'*, *C'*, and *D'* corresponding to those of Fig. 2 are at lower temperatures, showing that the lower dissociation pressures of the successive compounds are reached at lower temperatures, as would be expected, and further inflections, points *E'* and *F'*, were observed. The compositions of the condensed phase, assuming it to be non-volatile, for these points are given in Table 3.

TABLE 3.

	FIG. 2 (I)			FIG. 2 (II)		
Point	Composition	Pressure (mm.)	Temp.	Composition	Pressure (mm.)	Temp.
A, A'	$Me_2Be(PMe_3)_{2\ 01}$	94	32°	$Me_2Be(PMe_3)_{2\cdot00}$	60	20°
B, B'	$(Me_2Be)_2(PMe_3)_{3\cdot00}$	108	42	$(Me_2Be)_2(PMe_3)_{2\cdot84}$	74	29
C, C'	$Me_2Be(PMe_3)_{1\cdot05}$	131	75	$Me_2Be(PMe_3)_{1\cdot08}$	93	70
D, D'	$(Me_2Be)_3(PMe_3)_{1\cdot89}$	148	94	$(Me_2Be)_3(PMe_3)_{2\cdot04}$	106	80
E	—	—	—	$(Me_2Be)_4(PMe_3)_{2\cdot09}$	112	90
F'	—	—	—	$(Me_2Be)_5(PMe_3)_{1\cdot84}$	120	104

Some attempts were made to establish the composition of these compounds by experiments at constant temperature and variable pressure. Again the composition of the condensed phase was determined from the total amount of trimethylphosphine put in the high-temperature bulb less the N.T.P. volume of trimethylphosphine vapour at any given pressure. This procedure was also complicated by the melting or freezing of the condensed phase which occurred under some conditions when the pressure was altered. Moreover, the time taken for the establishment of equilibrium, particularly with a solid phase, was excessive. However, from isotherms at 25° and 50° the existence of the compounds Me_2Be,PMe_3 and $(Me_2Be)_3(PMe_3)_2$ was definitely demonstrated since the composition of the solid remained constant in these instances over quite a wide range of pressure. The 25° isotherm gave a dissociation pressure of 5·5 mm. for the 1 : 1, and 80—82 mm. for the 2 : 3 compound.

In view of the uncertainties mentioned above, and the smaller inflections observed at higher temperatures, considerably less reliance should be placed on the formulæ of the compounds containing the smaller ratios of phosphorus to beryllium, but at least the first four compounds of Table 3 appear quite definite. The observed succession of melting and freezing over the entire temperature range studied does, however, very strongly suggest that a series of compounds is formed: $Me_2Be(PMe_3)_2$, $(Me_2Be)_2(PMe_3)_3$, Me_2Be,PMe_3 or $(Me_2Be)_2(PMe_3)_2$, $(Me_2Be)_3(PMe_3)_2$, $(Me_2Be)_4(PMe_3)_2$, and $(Me_2Be)_5(PMe_3)_2$.

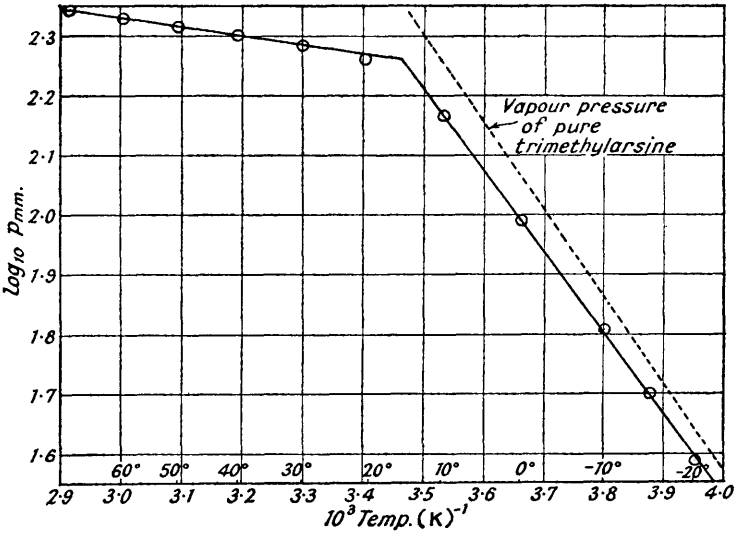
At low temperatures (−20° to −38°) and at pressures below the saturation pressure of trimethylphosphine, so that liquid trimethylphosphine was present, the vapour pressure observed was less than that of the pure phosphine since it contained some dissolved co-ordination compound, no doubt $Me_2Be(PMe_3)_2$.

Trimethylarsine.—Dimethylberyllium (21·0N-c.c.) and trimethylarsine (42·5N-c.c.) were condensed in the high-temperature bulb. No reaction appeared to take place, except that dimethylberyllium seemed to dissolve slightly in the arsine. As long as liquid trimethylarsine was present the pressure (Fig. 3) was slightly below the vapour pressure of pure trimethylarsine.

as would be expected if some dimethylberyllium was dissolved in it. At higher temperatures the variation of pressure with temperature followed the gas law, and the volume of gas present was 42·0 N-c.c., indicating no combination with the solid dimethylberyllium.

Dimethyl Ether.—The reaction between dimethylberyllium and an excess of dimethyl ether took place when the high-temperature bulb warmed to 5°, whereupon the former slowly liquefied. On cooling, the liquid product formed transparent crystals, which, in several experiments, began to melt at 5·0—5·5°, with sudden increase of pressure, and became entirely liquid at 9—10°. Two such experiments are represented in Fig. 4, in which plot I refers to a system containing 10·4N-c.c. of dimethylberyllium and 48·1N-c.c. of dimethyl ether, and for II the quantities were 14·3 and 65·6 respectively. In no case was the composition of the solid (m. p. 5—10°) constant; it varied between $Me_2Be(OMe_2)_{1·68}$ and $Me_2Be(OMe_2)_{1·8}$. This contrasts with the experiments with trimethylphosphine, in which the composition of the solid formed at low temperatures was always very close to the ratio 1 : 2. The composition of the liquid obtained on melting this solid (points *A* and *A′*) was, however, always close to $(Me_2Be)_2(OMe_2)_3$. On further heating, this liquid gradually dissociated until its composition, points *B* and *B′*, was Me_2Be,OMe_2, and then decomposed into its components, points *C* and *C′*, without any sign of the formation of compounds with a higher Be : O ratio. At lower pressures of dimethyl ether such compounds are formed. Fig. 5 represents two experiments in which 24·5N-c.c. of dimethylberyllium and 48·9N-c.c. (plot I) and 23·0N-c.c. (plot II) of dimethyl ether were present. In plot I the composition of the solid stable from −3° down to −30° or below, point *A* and to the right (measurements could not be made at much lower temperatures since the mercury would freeze), was constant at $Me_2Be(OMe_2)_{0·98}$, *i.e.*, a 1 : 1 compound within experimental error. This began to decompose above −5° and melted between 10° and 15° with evolution of dimethyl ether; decomposition continued until the composition of the liquid was close to $(Me_2Be)_2OMe_2$; at 43° (point *B*) the liquid was suddenly transformed into solid dimethylberyllium with evolution of all the dimethyl ether (the volume of gas then being 48N-c.c., point *C* and to the left).

FIG. 3. *Dimethylberyllium* (21·0N-c.c.) + *trimethylarsine* (42·5N-c.c.).



In plot II (23·0N-c.c. OMe_2) the condensed phase was solid at all temperatures. Over the temperature range −5° to +10° the volume of gas present was constant at 14·9N-c.c. (point *D* and to the right); thus 23·0—14·9 or 8·1N-c.c. of dimethyl ether were combined with 24·5N-c.c. of dimethylberyllium; thus the composition of the solid was $(Me_2Be)_3OMe_2$, or, as discussed below, more probably $(Me_2Be)_6(OMe_2)_2$. This compound began to decompose abruptly at 17° and above 30° (point *E* and to the left) the bulb contained only solid dimethylberyllium and gaseous dimethyl ether (23·0N-c.c.). The slope of the linear part of plot II corresponds to a heat of dissociation of approximately 9 kcal. per mole of dimethyl ether.

The compositions of the condensed phases represented by *A, B, C, A′, B′, C′* on Fig. 4 and *A, B, D* on Fig. 5, and corresponding temperatures and pressures, are given in Table 4. From these results it appears that the compounds $(Me_2Be)_2(OMe_2)_3$, Me_2Be,OMe_2, $(Me_2Be)_2OMe_2$, and $(Me_2Be)_3OMe_2$ are formed. These are much less stable than the trimethylphosphine compounds since they dissociate at considerably lower temperatures.

FIG. 4. *Dimethylberyllium and dimethyl ether.*

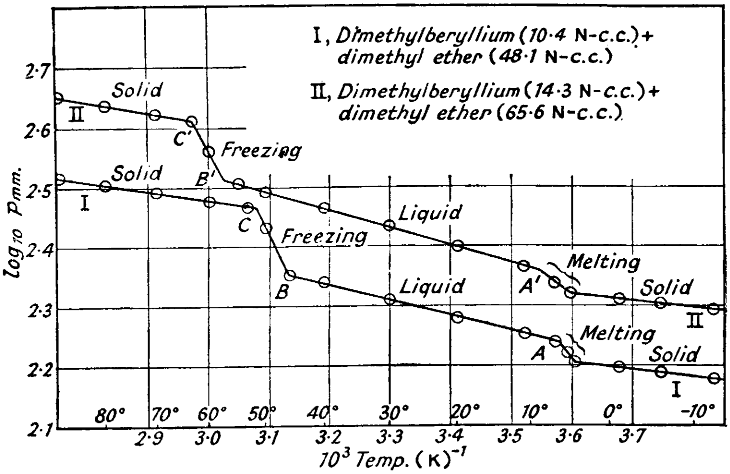
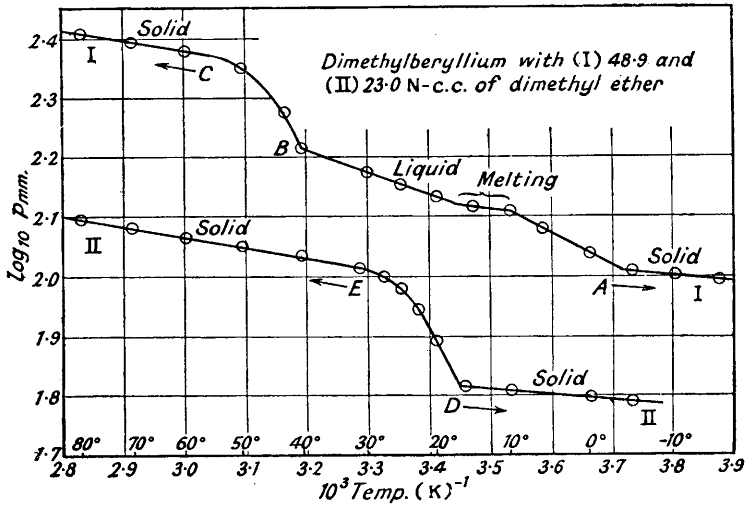


FIG. 5. *Dimethylberyllium and dimethyl ether.*



Diethyl Ether.—A smaller number of experiments was carried out with diethyl ether. At low temperatures, when liquid ether was present, its vapour pressure was somewhat less than that of pure ether on account of the solution of dimethylberyllium–ether complexes in the liquid. At higher temperatures and at pressures below the saturation pressure of ether, solid gradually separated as the temperature rose, with steady evolution of ether into the gas phase. In one

TABLE 4.

FIG. 4

Point	Composition	Pressure (mm.)	Temp.
A	$(Me_2Be)_2(OMe)_{2\cdot96}$	172	6°
A'	$(Me_2Be)_2(OMe_2)_{3\cdot10}$	231	11
B	$Me_2Be(OMe_2)_{1\cdot01}$	224	46
B'	$Me_2Be(OMe_2)_{0\cdot98}$	326	57
C	$(Me_2Be)_n$	290	52
C'	$(Me_2Be)_n$	410	63

FIG. 5

Point	Composition	Pressure (mm.)	Temp.
A	$Me_2Be(OMe_2)_{0\cdot98}$	102	−3°
B	$(Me_2Be)_2(OMe_2)_{1\cdot07}$	164	43
D	$(Me_2Be)_{3\cdot02}OMe_2$	65	17

experiment with 19·5N-c.c. of dimethylberyllium and 39·1N-c.c. of diethyl ether, the condensed phase was solid from 20° to just over 40°, the solid then suddenly decomposing to dimethylberyllium, with an increase in pressure from 127 to 173 mm. over a 5° temperature range. There was no indication of the formation of compounds of definite composition.

Dimethyl Sulphide.—When the high-temperature bulb contained dimethylberyllium and dimethyl sulphide, the volume (N-c.c.) of the latter at all temperatures from 20° (pressure 163 mm.) to 110° (pressure 217 mm.) was the same as the volume initially added; thus no reaction took place.

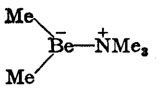
DISCUSSION

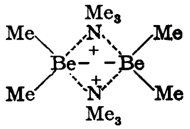
Relative Donor Properties.—Of the donor compounds studied only trimethylamine gave a co-ordination compound with dimethylberyllium from which the donor molecule could not be removed by pumping in a high vacuum at room temperature. This compound, Me_2Be,NMe_3, was stable as vapour to at least 180°. The compounds with trimethylphosphine all decomposed on pumping at room temperature, so did the dimethyl ether complexes; the former, however, were stable to considerably higher temperatures than the latter. Thus the 2 : 1 compound $(Me_2Be)_2PMe_3$, point *E'* of Fig. 2 (II), melts and begins to decompose at 90° under a pressure of 112 mm. of trimethylphosphine, while the corresponding oxygen compound $(Me_2Be)_2OMe_2$, point *B* of Fig. 5, decomposes at 43° under a pressure of 164 mm. of dimethyl ether. Since neither dimethyl sulphide nor trimethylarsine reacts, the order of donor properties towards dimethylberyllium is :

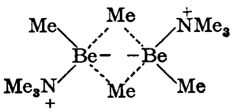
$$NMe_3 > PMe_3 > OMe_2 > AsMe_3, SMe_2 = 0.$$

This order is the same as that found with trimethylaluminium (Brown and Davidson, *J. Amer. Chem. Soc.*, 1942, **64**, 316) and trimethylgallium (Coates, *J.*, 1951, 2003); it is the order to be expected when the acceptor atom is of the type that forms simple co-ordinate links without complication due to double bonding or any similar influence of *d* orbitals.

Nature of the Co-ordination Compounds of Dimethylberyllium.—Dimethylberyllium–trimethylamine. This is the only known example of a metal co-ordination compound, sufficiently stable to exist in the gaseous state, in which the metal has the rather unusual co-ordination number of *three.* One may assume that the beryllium atom assumes the sp^2 orbital grouping, giving a planar molecule. The compound might be dimeric in the condensed state, and its insolubility in benzene prevented molecular-weight measurements in solution (other, generally either donor or otherwise reactive solvents, are best avoided with this class of substance). The observed quite unusually large variation of its latent heat of vaporisation with temperature, from about 12 kcal./mole at 50° to about 8 at 130° is, however, a hint that an equilibrium such as monomer $\rightleftharpoons$ dimer may obtain in the liquid, and is consistent with the presence of a high proportion of dimer (higher L_V) at lower temperatures and of monomer (lower L_V) at higher temperatures. The structure of the solid dimethylberyllium–trimethylamine compound, which could only be resolved by *X*-ray analysis, is thus a matter of some interest, since there are at least three reasonable possibilities, *viz.*,



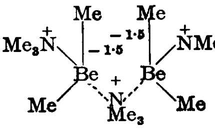




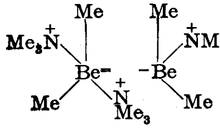
In these and other formulæ, a broken line has an exact significance and represents a half-bond.

Bisdimethylberyllium–tristrimethylamine. This compound was not obtained as a gas, so it is not certain that it is monomeric. It is, however, difficult to see how it could be associated. The nature of the bonding in it is rather obscure, but one possibility is that two Me_2Be,NMe_3 units are bonded together by means of one trimethylamine molecule. The general chemistry of beryllium reveals a very strong tendency towards the formation of four tetrahedrally disposed covalent bonds; this is illustrated, for example, by the $BeF_4^=$ ion, basic beryllium acetate, and the beryllium acetylacetone compound. The same tendency manifests itself in solid dimethylberyllium (see Part I and below), an electron-deficient structure in which the beryllium forms essentially four half-bonds.

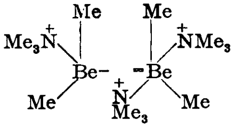
It is now suggested that a somewhat similar type of bonding is present in the compound $(Me_2Be)_2(NMe_3)_3$:



(*a*)



(*b*)

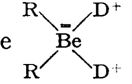


(*c*)

Structure (*a*) is regarded as equivalent to the two "resonance" forms (*b*) and (*c*), but is preferred. The formal charges on the beryllium and nitrogen atoms would correspond to complete symmetry of the molecular orbitals, *i.e.*, each bond having no bond dipole moment. Differences of electronegativity would, of course, reduce these charges by a molecular-orbital asymmetry in the sense of a greater electron density at the more electronegative (*i.e.*, C or N) end of each bond to beryllium. The Be–N–Be bond is regarded as consisting of one molecular orbital, doubly occupied, derived from one tetrahedral orbital from each beryllium atom and one from the central nitrogen atom, just as the B–H–B bond in diborane is generally regarded as derived from one tetrahedral orbital from each boron and one 1*s* hydrogen orbital.

The main objections to this proposed structure are (*a*) that it would seem difficult, on stereochemical grounds, for the beryllium atoms to approach sufficiently close to the nitrogen atom, which must be fairly obstructed by the three methyl groups, although it must be remembered that half bonds are substantially longer than whole bonds, and (*b*) that this would be the only example of nitrogen with a co-ordination number of five.* In this class of compound, however, there is ample evidence that carbon can attain this co-ordination number, and Gillespie (*J.*, 1952, 1002) has suggested on theoretical grounds that nitrogen may possibly do likewise.

The trimethylphosphine compounds. There is clear evidence for the formation of compounds with Be : P ratios of 1 : 2, 2 : 3, 1 : 1, and 3 : 2, with somewhat less reliable evidence for the formulæ of compounds with higher Be : P ratios, but little doubt as to their existence. In one way the simplest to interpret is the 1 : 2 compound $Me_2Be(PMe_3)_2$, since this represents beryllium achieving its stable co-ordination number of four without any need to invoke half-bonds. On the other hand, one must enquire why such a compound was not formed by trimethylamine, which is a considerably stronger donor molecule. It may possibly have been due to wrong experimental conditions, but this is unlikely since the compound $(Me_2Be)_2(NMe_3)_3$ persisted down to −30° in the presence of free trimethylamine. The failure to prepare a compound $Me_2Be(NMe_3)_2$ is unlikely to be due to steric interference between the trimethylamine molecules—such interference would be even greater in the bistrimethylphosphine compound, and moreover the compound $Me_3C{\cdot}CMe_2{\cdot}CMe_3$, which should have much the same size and shape, is quite stable. Beryllium is a relatively electropositive element (electronegativity 1·5 on the Pauling scale) and may not be able to combine with two donor molecules forming a compound of structure



$R_2\overset{=}{Be}(D^+)_2$

in which D represents a donor molecule, unless the atoms bonded to beryllium are so electronegative that the resulting polarity of the bonds effectively removes much of this double negative charge from the beryllium atom. This would be so in the case of the numerous co-ordination compounds of beryllium chloride of the type Cl_2BeD_2 (reviewed by Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, pp. 208—213), chlorine being a highly electronegative element; in the case of dimethylberyllium, where R = Me, the atoms bonded to the beryllium may not be sufficiently electronegative. The problem then takes the form of why a 1 : 2 compound $Me_2Be(PMe_3)_2$ is obtained, particularly since phosphorus is a less electronegative element than nitrogen. Now one of the more

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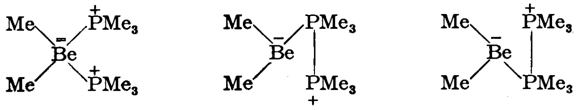
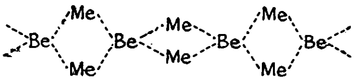
* The authors are indebted to a Referee for these points.

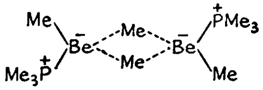
important differences between phosphorus and nitrogen is that the maximum covalency of the former is not limited to four, and it is tentatively suggested that, just as the P–O bond in phosphine oxides is less polar than the N–O bond in amine oxides owing to the possibility of a covalency of five for phosphorus, $R_3P{=}O$, the compound dimethylberyllium–bistrimethylphosphine may be represented by the following structures:



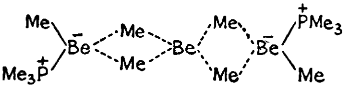
For there to be appreciable P–P bonding it would be necessary for the P–Be–P angle to be somewhat less than 109°. The second and third of the above structures would not be



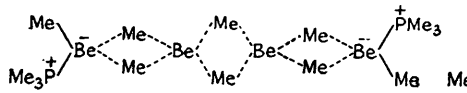
(A)



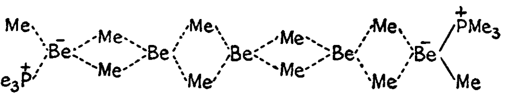
(B)



(C)



(D)



(E)

possible with nitrogen or oxygen as donor atoms, and it will be recalled that no compound $Me_2Be(OMe_2)_2$ was obtained.

The existence of the remaining compounds, *viz.*, $(Me_2Be)_3(PMe_3)_2$, $(Me_2Be)_2PMe_3$, and $(Me_2Be)_5(PMe_3)_2$, becomes intelligible on recalling the structure (*A*) of dimethylberyllium itself, since donor molecules would provide a very simple means for ending this polymeric chain. Therefore it is suggested that these compounds and probably also the 1 : 1 complex have the constitutions (*B*—*E*). The compound $(Me_2Be)_2PMe_3$ may in this way be regarded as $(Me_2Be)_4(PMe_3)_2$, but there may be some doubt about the 1 : 1 compound, for which, as for the other trimethylphosphine complexes, there is no evidence of molecular weight. It may have the above structure, or it may be monomeric like the trimethylamine compound $Me_2\overset{-}{Be}\text{–}\overset{+}{N}Me_3$, but evidence in favour of the dimeric formula is presented later.

Ether compounds. The observed compounds formed by dimethyl ether are consistent with the views set out above. No bisether complex could be obtained; this could be due either to the weaker donor character of dimethyl ether than of trimethylphosphine, or to the reasons (applicable equally to ether) advanced to show why no bistrimethylamine compound was formed, or to both these reasons. The compounds $(Me_2Be)_2(OMe_2)_3$, Me_2Be,OMe_2, $(Me_2Be)_2OMe_2$, and $(Me_2Be)_3OMe_2$ are regarded as similar to the analogous trimethylphosphine compounds.

Heats of Co-ordination.—It is possible to make approximate estimates of the heat of formation of co-ordinate bonds to beryllium. Reaction (1) occurs spontaneously at room temperature, and the dissociation pressure of trimethylamine was quite undetectable and may be considered as less than 10^{-4} atmosphere. Hence the free-energy change $\Delta G_1{}^{\circ} < -5{\cdot}5$ kcal./mole. Since the major part of the entropy change, $\Delta S_1{}^{\circ}$, must be due to the

$$\mathrm{Me_2Be(s,\ polymer) + NMe_3(g) \longrightarrow Me_2Be,NMe_3(s)} \qquad (1)$$

$$\mathrm{Me_2Be(s,\ polymer) \longrightarrow Me_2Be(g,\ monomer)} \qquad (2)$$

$$\mathrm{Me_2Be,NMe_3(s) \longrightarrow Me_2Be,NMe_3(g)} \qquad (3)$$

$$\mathrm{Me_2Be(g,\ monomer) + NMe_3(g) \longrightarrow Me_2Be,NMe_3(g)} \qquad (4)$$

disappearance of the translational entropy of a mole of trimethylamine, which is 38 e.u. at 25° and 1 atm., one may conclude that $\Delta S_1 \approx -40$. Hence ΔH_1 must be $< -(5{\cdot}5 - 40) \times 300$ or $< -17{\cdot}5$ kcal./mole. Since $\Delta H_2 = 23{\cdot}5 \pm 2$ kcal./mole of monomer (from Part I, but there is some uncertainty about extrapolation to room temperature from 150—180°, at which ΔH_2 was measured), and $\Delta H_3 = 20 \pm 1$ (this paper), it follows that $\Delta H_4 = \Delta H_1 + \Delta H_3 - \Delta H_2 < -21 \pm 3$. The corresponding heat terms for the co-ordination of trimethylamine to trimethylboron (Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2923) and trimethylgallium (Coates, unpublished observation) are —17·6 and —21·0 kcal./mole respectively. Trimethylaluminium–trimethylamine (Brown and Davidson, *loc. cit.*) was too stable to permit measurement of dissociation equilibria, therefore $\Delta H < -21$ kcal., as for the beryllium compound discussed above. Hence it appears that the relative acceptor properties of these elements are in the order B < Ga < Al,Be.

The dissociation pressure of $(Me_2Be)_2(NMe_3)_3$, for which a half-bonded structure has been suggested, appears to be somewhat less than 0·1 atm. at 25°, hence ΔG° for the reaction $(Me_2Be)_2(NMe_3)_3 \longrightarrow 2Me_2Be,NMe_3 + NMe_3$ is $\sim +(1-2)$ kcal./mole. When similar assumptions (as above) are made about the entropy change, ΔH becomes about —14 kcal./mole; thus the heat of co-ordination of one mole of trimethylamine to two moles of Me_2Be,NMe_3, by—it is suggested—two half-bonds, is of the order of 14 kcal.

From Fig. 2 and Table 3 it appears that the dissociation pressures for equilibria of the type

$$(n + 1)(Me_2Be)_n(PMe_3)_2 \rightleftharpoons n(Me_2Be)_{n+1}(PMe_3)_2 + 2PMe_3$$

where $n = 3$, 4, or 5, are of the order of 100 mm. at 80°. Thus $\Delta G^\circ \approx 1$ kcal./mole of PMe_3, and, when similar assumptions are made for ΔS°, $\Delta H^\circ \approx -15$. On the basis of the structures, proposed above, of these compounds, ΔH° would be roughly the heat of co-ordination of one trimethylphosphine molecule to the dimethylberyllium polymer, less the heat required to convert two beryllium–carbon half-bonds into one whole bond. The latter quantity was estimated in Part I as about 11 kcal. for short polymers, hence the required heat of co-ordination is approximately 26 kcal./mole of PMe_3. A similar calculation based on the observed dissociation pressure of $(Me_2Be)_2(PMe_3)_2$, 5·5 mm. at 25°, leads to an identical value for the heat of co-ordination. It is interesting that, if the above compound is regarded as Me_2Be,PMe_3, a value of ~ 58 kcal. is obtained for the heat of co-ordination; this impossible value provides evidence in favour of the dimeric structure, a conclusion which cannot be altered unless wildly improbable entropy changes for the solids are assumed.

Although dimethyl sulphide forms quite a stable co-ordination compound with trimethylaluminium ($\Delta H = -19$ kcal./mole; Brown and Davidson, *loc. cit.*), it does not react with dimethylberyllium. On the supposition that the heat of co-ordination of dimethyl sulphide to dimethylberyllium is the same as to trimethylaluminium, a reversal of the type of calculation given above leads to a dissociation pressure of 200—300 atmospheres for the dimethylberyllium–dimethyl sulphide system (a result in agreement with the reported failure to observe such compounds).

Although dimethylberyllium is undoubtedly a very strong acceptor, as would be expected in view of the highly electron-deficient structure of the solid polymer, the formation of co-ordination compounds and their nature are highly sensitive to the heat of co-ordination. In conclusion, it appears that co-ordination compounds are formed only if the heat of co-ordination per mole of donor is at least 10—11 kcal. greater than the heat required to form one Be–C whole bond from two half-bonds, *i.e.*, >*ca.* 21—22 kcal. Thus we arrive at the following approximate estimate of heats of co-ordination to dimethylberyllium : S, As < 21; 21—22 < O < 25—26; P $\sim$ 26; N > 26 kcal.

Finally, there appears to be only one parallel to the behaviour of dimethylberyllium with donor molecules. Stecher and Wiberg (*Ber.*, 1942, **75**, 2003) found that aluminium hydride, which clearly has a polymeric structure $(AlH_3)_n$ (Longuet-Higgins, *J.*, 1946, 139), reacts with trimethylamine in a complex manner. Slightly volatile mixed crystals of $AlH_3,NMe_3 + AlH_3,2NMe_3$ are described, from which were prepared, under suitable conditions of temperature and partial pressure of trimethylamine, compounds of approximate compositions AlH_3,NMe_3, $(AlH_3)_3,NMe_3$ and $(AlH_3)_5,NMe_3$. Thus the behaviour of trimethylamine with aluminium hydride appears to be intermediate in character between that of trimethylamine and trimethylphosphine towards dimethylberyllium.

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